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σ-Noninnocence: Masked Phenyl-Cation Transfer at Formal Ni^{IV}

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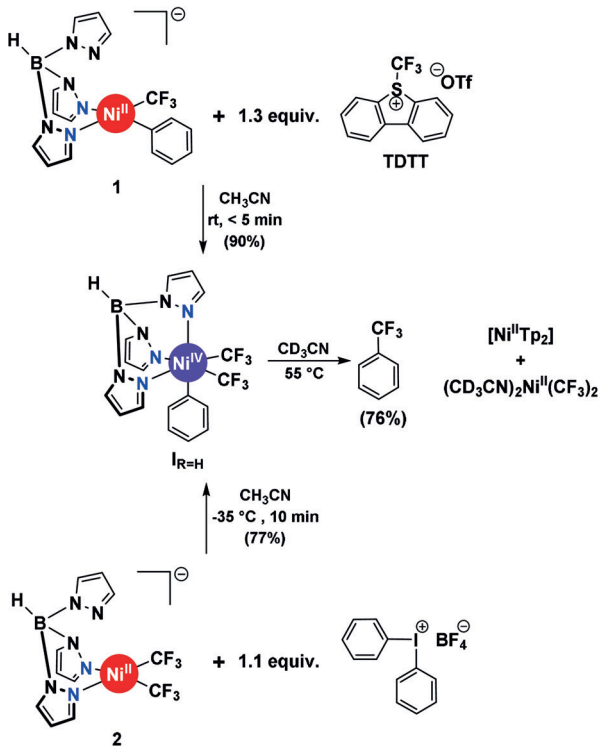
Abstract: *Reductive elimination is an elementary organometallic reaction step involving a formal oxidation state change of −2 at a transition-metal center. For a series of formal high-valent Ni^{IV} complexes, aryl–CF_3 bond-forming reductive elimination was reported to occur readily (Bour et al. J. Am. Chem. Soc.* ***2015****, 137, 8034–8037). We report a computational analysis of this reaction and find that, unexpectedly, the formal Ni^{IV} centers are better described as approaching a +II oxidation state, originating from highly covalent metal–ligand bonds, a phenomenon attributable to σ-noninnocence. A direct consequence is that the elimination of aryl–CF_3 products occurs in an essentially redox-neutral fashion, as opposed to a reductive elimination. This is supported by an electron flow analysis which shows that an anionic CF_3 group is transferred to an electrophilic aryl group. The uncovered role of σ-noninnocence in metal–ligand bonding, and of an essentially redox-neutral elimination as an elementary organometallic reaction step, may constitute concepts of broad relevance to organometallic chemistry.*

Introduction

Several studies propose the involvement of high-valent Ni^{IV} intermediates in nickel-catalyzed cross-coupling reactions.[1] A high-yielding aryl–CF_3 bond formation from well-defined Ni^{IV} complexes $\mathbf{I_{R=H}}$ has recently been reported by the group of Sanford (Scheme 1).[2] These formal Ni^{IV} complexes bear two trifluoromethyl ligands and are readily accessible from Ni^{II} precursors via two distinct synthetic routes, either through oxidation with an electrophilic CF_3 transfer reagent (*S*-(trifluoromethyl)dibenzothiophenium triflate, TDTT) or an aryl group from a diaryl iodonium salt.[2] The Ni center is supported by the anionic trispyrazolylborate (Tp) ligand which changes from two- to three-coordinate as either the CF_3 or Ar group is introduced. A Hammett analysis



Scheme 1. Reported synthesis of the Ni^{IV} complex $\mathbf{I_{R=H}}$ by Sanford and co-workers via oxidation of **1** with TDTT (top), or via reaction of **2** with Ph_2IBF_4 (bottom), and its subsequent aryl trifluoromethyl bond-forming reductive elimination (center).[2]

of the aryl–CF_3 bond-forming reductive elimination from $\mathbf{I_{R=H}}$ suggests that the reaction proceeds via a nucleophilic attack of the aryl ligand on an electrophilic CF_3 ligand. We became interested in these findings as these high-valent formal Ni^{IV} species have become suspect of featuring an inverted ligand field,[3] rendering the assignment of oxidation states in these complexes possibly challenging.[4]

The concept of inverted ligand fields was recently reviewed by Hoffmann et al.[5] and is most prominently discussed for the prototypical example of the $[Cu(CF_3)_4]^-$ anion.[3a,6] Already in 1995, Snyder proposed that this formal $Cu^{III}(d^8)$ complex would be better described as a $Cu^{I}(d^{10})$ complex.[6a] Snyder originally proposed this to reflect the presence of an oxidized ligand as shown in Figure 1, top. Notably, all valence tautomers have to be taken into account, leading to a partial oxidation of all CF_3 groups. While controversial at the time,[6b,c] recent studies confirmed Snyder's proposal through spectroscopic evidence verifying the near-complete occupation of all five 3d orbitals.[3a,6e] In these complexes, unlike in conventional cases (that is, Werner-type complexes such as $[Rh(CO)_4]^+$), the amount of metal

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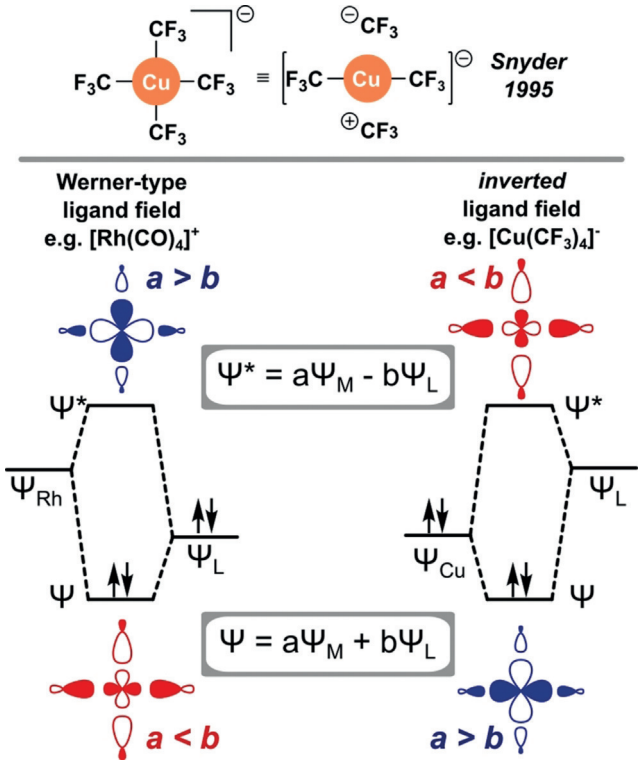

Figure 1. Top: Snyder's originally proposed oxidation state assignment for the $[Cu(CF_3)_4]^-$ anion (for the original proposal, see Ref. [6a]). Bottom: Conceptual depiction of the changes to the metal–ligand bonding due to the presence of an inverted ligand field (Adapted with permission from Ref. [3a, 5a]. Copyright 2016 American Chemical Society).

character vs. ligand character to the bonding and antibonding orbitals are inverted: for the $[Cu(CF_3)_4]^-$ anion, an unoccupied metal–ligand antibonding orbital is mainly of ligand character, whereas the corresponding occupied bonding orbital is mainly of metal-d-orbital character (see Figure 1, bottom; for a detailed discussion, see Refs. [3a, 5a]). This leads to ligand oxidation and hence the presence of a formal and notably electrophilic „CF_3^{+}“,[5a] which originates from highly covalent metal–ligand σ-bonds. A recent study by Menjón and co-workers extended this interpretation of reduced oxidation states at the metal center to the $[Ag(CF_3)_4]^-$ and $[Au(CF_3)_4]^-$ anions.[7] However, it should be noted that these earlier studies proposed the bonding model shown in Figure 1 primarily via formal molecular-orbital-theory considerations and generally identify the bonding and antibonding orbitals in Figure 1. We will argue below that this is often inappropriate in larger complexes or complexes of little symmetry, and that such considerations should be based on occupied and unoccupied localized valence molecular orbitals instead, rather than canonical molecular orbitals as presently done.

As metal–ligand σ-bonding becomes increasingly covalent, a clear attribution from an oxidation state point of view becomes challenging.[8] Notably, Hoffmann et al. have also used the term σ-noninnocence when discussing complexes that feature increased covalency, leading to ambiguity in attributing oxidation states.[5a] We shall note here that non-innocence has already been introduced as a concept some time ago,[9] however, it usually refers to difficulties in assigning oxidation states due to ambiguity in the occupation of π-orbitals present in ligands.[10]

Interestingly, in several instances, high-valent Ni complexes have been implicated to feature inverted ligand fields[3b,c,6d] and thus may also be affected by σ-noninnocence, and, as a consequence, lead to a blurry oxidation state assignment. With this in mind, we commenced a computational study to shed light on the electronic configuration and reactivity of the intriguing Ni^{IV} complexes shown in Scheme 1. In our study, we will focus on two aspects: i) the oxidation state of the Ni center and the ligands, and ii) how the reactivity is affected by the electronic structure.

Results and Discussion

We begin by investigating the oxidation state of the Ni center and the adjacent ligands. For this purpose, we first optimized the geometry of complex $\mathbf{I_{R=H}}$ using the M06-L[11]/def2-SVP[12] method in combination with the SMD[13] solvation model for MeCN (full computational details can be found in the Supporting Information). We next applied Salvador's effective oxidation state (EOS) formalism,[14] where we fragment the complexes into the Ni center, two individual CF_3 groups, the aryl moiety, and the anionic trispyrazolylborate (Tp) ligand. For this purpose, we computed the Kohn–Sham wave function with the M06-L[11] functional in combination with the larger basis set def2-TZVPPD[12,15] and the SMD[13] solvation model for MeCN. Consistent with the suspicion that σ-noninnocence could be at play for these complexes, we found in all cases that the formal Ni^{IV} center is more appropriately described as a two-electron reduced Ni^{II} site (see Table S1 in the Supporting Information). Based on the experimental Hammett plot reported by Sanford and co-workers, we would expect that the CF_3 group should be oxidized, since a negative slope of the Hammett analysis suggests the transfer of an electrophilic CF_3 group (see below). However, to our surprise, this is not the case and each CF_3 group is predicted to be anionic. It is indeed the aryl moiety that is predicted to feature an overall oxidation state of +I and thus provides two electrons to the Ni center. The Tp ligand features an oxidation state of −I, consistent with its anionic nature. While the description of a reduced Ni center is in agreement with the careful suggestions made for high-valent Ni complexes in the literature,[3b,c,6d] the assignment of a cationic aryl moiety, however, conflicts with the experimental study reported by Sanford and co-workers. In a Hammett analysis of the aryl–CF_3 reductive elimination, a linear correlation with a slope of −0.91 was found, supporting the idea of the reaction between an aryl anion and a cationic CF_3 group.[16] In particular, the interpretation involving an electrophilic CF_3 moiety is therefore not in agreement with the oxidation state assignment obtained from the EOS analysis. Although the EOS analysis only provides integer values for oxidation states, it does probe the reliability of the assignment, which is expressed as the R value which can range from 50–100 %.[14] In the present case, we obtained

a low value of 55%, suggesting that the elucidation of the oxidation state is challenging and further supporting that noninnocence is at play (see also Table S1).

In principle, by producing a molecular-orbital (MO) description of the electronic structure of the ground state, one should be able to uncover a ligand-field inversion based on the degree of covalency of the metal–ligand bonding interactions and the increased ligand character of the unoccupied antibonding orbitals (see above). In structurally simple complexes such as four-coordinate square-planar complexes with high symmetry (for example, $[Cu(CF_3)_4]^-$), this antibonding orbital can often be associated with the LUMO as obtained from a first-principles calculation (qualitatively shown in Figure 1).[5a] However, for six-coordinate systems, such as Sanford's Ni^{IV} complexes, the additional dimension and lower symmetry render this task more challenging, and the actual HOMOs and LUMOs from first-principles calculations are generally delocalized and complex in shape, and do not clearly correspond to either bonding picture in Figure 1; often enough, they do not even have substantial metal character. We will therefore use the intrinsic bond orbital (IBO) method[17] for the interpretation of the bonding in these complexes, a method we have successfully used for the analysis of bonding in transition-metal complexes before.[18] With this approach, we are able to transform the delocalized molecular orbitals into chemically intuitive localized orbitals while retaining an exact representation of the Kohn–Sham wave function. In Figure 2, we show the d-orbitals of the Ni center and the metal–ligand bonding interactions.

At first glance, based on the number of doubly occupied d-orbitals, it seems apparent that the complex consists of a d^6 electron configuration and hence a Ni^{IV} metal ion (Figure 2, top). However, a closer look at the partial charge distribution of the metal–ligand bonding interactions reveals the origin of the EOS assignment as a Ni^{II} center and a cationic phenyl substituent. Here, interactions for the N–Ni bonding of the Tp ligand (Figure 2 A,E,F) are clearly dative in nature, since the partial charges mainly reside on the N (N: 1.745/1.715/1.715 and Ni: 0.117/0.181/0.181). For the two Ni–CF_3 interactions (Figure 2 B,C), the situation already changes significantly and partial charge distributions of 1.290/1.290 for C_{CF_3} and 0.657/0.657 for Ni are found, which indicate a transition to more covalent bonding. Notably, these bonds are still polarized towards the CF_3 ligand. This changes when we look at the bonding between C_{Ph} and Ni, where an inversion of the bond polarity is identified and the partial charge on Ni of 0.988 is larger than the one on C_{Ph} of 0.973 (Figure 2 D). We have also investigated this for a series of substituents on the aryl group and find very similar trends (Table S3), especially for the relative covalency observed for the aryl–Ni interaction and also find similar trends for group partial charges (Tables S4 and S5). The extreme covalency lies at the heart of the observation of σ-noninnocence. We may reiterate here that it was stated by Ye et al. that a clear assignment of oxidation states becomes increasingly difficult as covalency increases,[20] and thus, by definition, constitutes noninnocence. From the recent studies on inverted ligand fields, one can conclude that metal–CF_3 interactions are preferred (see above). However,

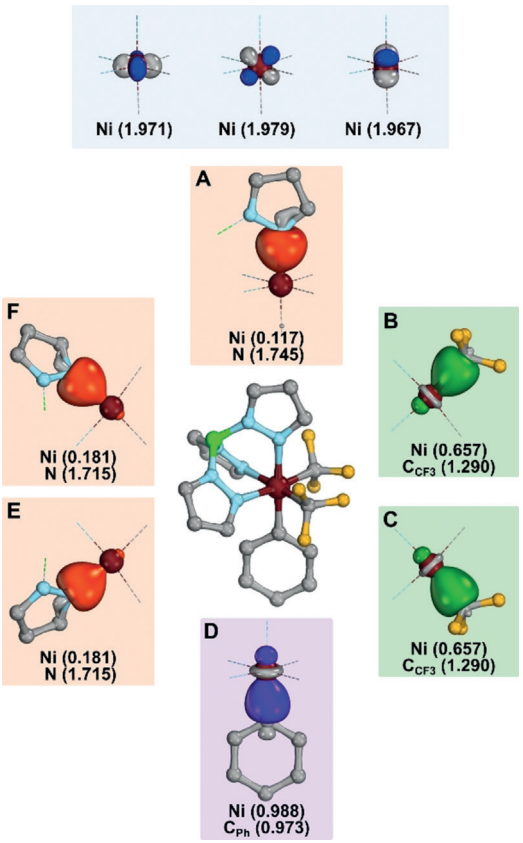

Figure 2. IBO depictions of three occupied d-orbitals (top) and six Ni–ligand-bonding IBOs. Numbers in parentheses indicate the partial-charge distribution of a given IBO at M06-L/def2-TZVPPD/SMD//M06-L/def2-SVP/SMD. Orbital iso-surfaces enclose 80% of the integrated electron density of the orbital. Hydrogen atoms are omitted for clarity. Depicted using IboView.[19]

our current findings clearly demonstrate that σ-noninnocence can arise from any covalent metal–ligand interaction. Throughout, we have discussed IBOs which are obtained by localization of all occupied MOs. Because the inspection of the virtual space is frequently used in the identification of inverted ligand fields, we will also introduce and discuss valence virtual IBOs (vvIBOs) here as a representative of the chemical unoccupied valence orbitals available in a system for chemical interactions (Technically, these are obtained straightforwardly by first computing a set of basis vectors for the orthogonal complement of the occupied space in the intrinsic atomic orbital space and then applying the standard IBO localization procedure to these basis vectors. For a short technical description of the IBO method, see also Ref. [18f]). In agreement with the general concept that the „LUMO"[21] should be ligand-centered when an inverted ligand field is present (see above), we can clearly identify the vvIBO that is antibonding in nature with regard to the Ni–C_{Ph} bond (Figure 3 A). Here, the virtual partial charge distribution at Ni is only 0.169, corresponding to 8.5% Ni character, which is in line with a ligand-centered vvIBO. In contrast, from the vacant 4s orbital, which—as expected—is almost exclusively Ni-centered (Figure 3 B), it can be seen that localization of the virtual space in combination with the virtual partial-

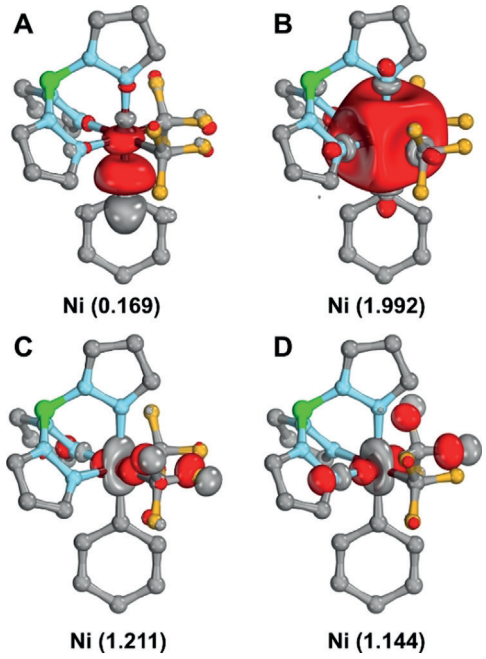

Figure 3. vvIBO depictions of $\mathbf{I}_{R=H}$. Numbers in parentheses indicate the virtual partial charge distribution at Ni of a given vvIBO at M06-L/def2-TZVPPD/SMD//M06-L/def2-SVP/SMD. Hydrogen atoms are omitted for clarity. Depicted using IboView.[19]

charge distribution can be used to identify metal/ligand character. The antibonding vvIBOs for the Ni–C_{CF_3} bonds remain metal-centered (Figure 3C,D), in line with our previous assignment that these remain anionic in nature. The inspection of vvIBOs is therefore consistent with our interpretation and further supports the assignment made thus far. We note that these localized occupied and virtual valence molecular orbitals (IBOs and vvIBOs, respectively), which represent the bonding and antibonding molecular orbitals associated with the metal, are also well defined in complex and non-symmetric coordination complexes, and are conceptually much closer related to a distinction of the bonding models illustrated in Figure 1 than the usually discussed HOMOs and LUMOs are. We here find that the use of vvIBOs provides a clear picture of the bonding scenarios and allows for the immediate evaluation of whether an inverted ligand field is present or not, even when highly delocalized MOs would render such an analysis challenging or inconclusive. In particular, the localized orbital description allows for the direct identification of which bond(s) is(are) affected by σ-noninnocence.

Having made our analysis above, it is now time to address the obvious inconsistency between our oxidation state assignment, that is, a cationic aryl ligand and anionic CF_3 groups, and the experimentally observed Hammett plot reported by Sanford and co-workers.[2] The transfer of an anionic CF_3 group to a Ni-bound aromatic moiety would constitute a nucleophilic-aromatic-substitution-type reaction and should result in a positive slope (for an example see Ref. [22]). The experimentally determined negative slope of −0.91 for complexes **I** clearly suggests the build-up of positive charge on the aromatic ring in the C–C bond-forming process.[23] Based on our bonding analysis however, we would expect that the CF_3 group is transferred as an anion to an electrophilic aromatic moiety. To probe which scenario is operational, we decided to follow the electron flow based on the changes that the IBOs undergo along the reaction path of the C–C bond-forming event, an approach we have used successfully before, even in challenging scenarios.[19b,24]

From this analysis, we can clearly identify that the IBO associated with the C_{Ph}–Ni bond is transformed into a Ni d-orbital and the IBO that describes the C_{CF_3}–Ni bond becomes the new C–C bond (Figure 4). The transformation of the C_{CF_3}–Ni bond into the C–C bond in the product is therefore clearly identified as a nucleophilic attack by the CF_3 ligand on an electrophilic aryl ligand. A plot of the root of the sum of square deviations (RSSD) of the partial-charge distribution changes along the IRC also shows that these transformations are continuous (Figure 5).

While these calculations are in full agreement with our original assignment of oxidation states (see above) they remain at conflict with the Hammett plot. One might wonder if our computational methodology is appropriate. Therefore,

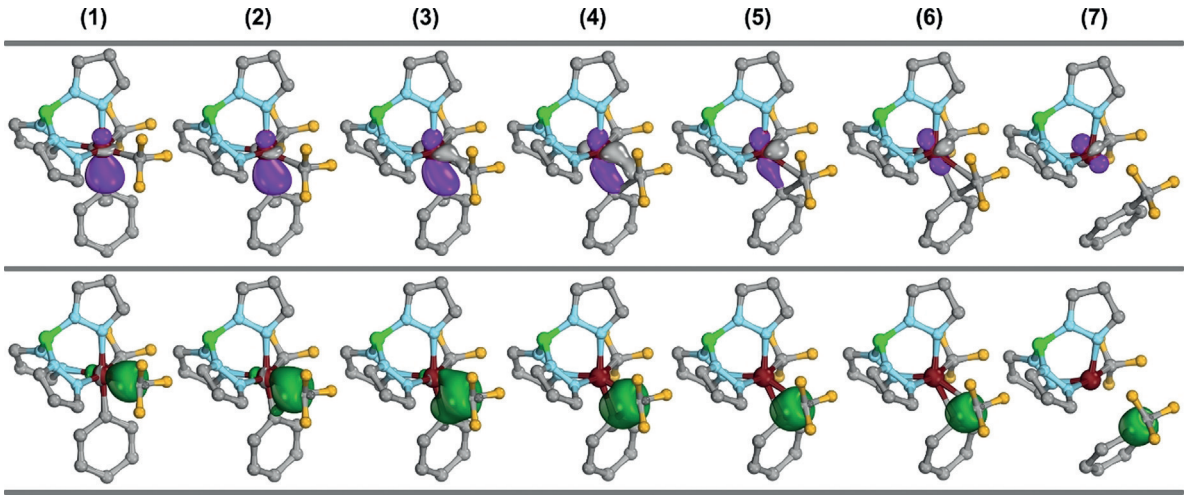

Figure 4. Depiction of the Ni–C_{Ph} (purple, top) and Ni-C_{CF_3} (green, bottom) IBOs along the IRC (M06-L/def2-SVP/SMD). For the position along the IRC, see Figure 5. Hydrogen atoms are omitted for clarity.

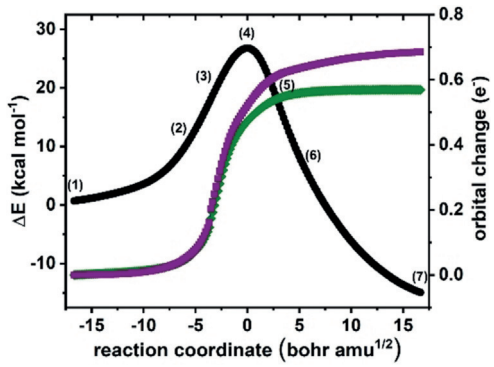

Figure 5. RSSD partial charge changes of the Ni–C_{Ph} (purple) and Ni–C_{CF_3} (green) IBOs along the IRC (M06-L/def2-SVP/SMD).

we computed the reductive elimination of all substituents used in the experimental Hammett plot. In agreement with the experimental data, we also observed a negative slope (Figure 6). While the slope of the computed Hammett plot is slightly larger in absolute value (−3.23), it clearly reproduces the experimental trends and thus we may conclude that our methodology is appropriate. We also note that the EOS analysis for all complexes $\mathbf{I_{R=X}}$ produces a Ni^{II} center, a cationic aromatic moiety, and anionic CF_3 groups along with very similar partial-charge distributions of the IBOs describing the Ni–ligand bonding (Tables S2 and S3). A closer

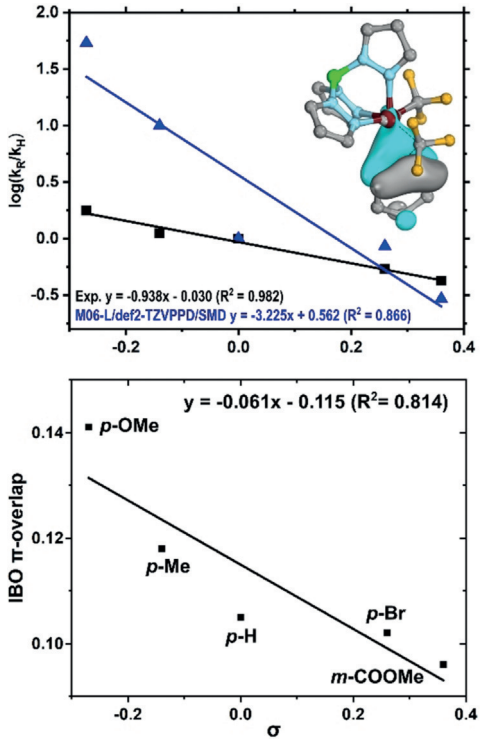

Figure 6. Top: Comparison of computed (blue triangles) and experimental (black squares) Hammett plots. Experimental data and Hammett parameters were taken from Ref. [2]. Inset: IBO overlap of the aromatic π-system with Ni at the transition state. Bottom: Plot of the IBO overlap of the aromatic π-system with Ni vs. Hammett σ-values.

inspection of the IBOs at the TS led to the identification of a crucial interaction in which the Ni center acts as a Lewis acid significantly activating the aromatic π-system (Figure 6, inset). The IBO overlap of the aromatic π-system with the Ni center increases with electron-donating substituents and thus stabilizes the TS, whereas it decreases with electron-withdrawing substituents (Figure 6, bottom, and Table S9). Notably, Fernández and Frenking found before that the π-conjugation strength in aromatic systems correlates well with Hammett σ-parameters.[25] As a consequence, we find that the interaction between the aromatic π-system, as quantified by the partial-charge overlap of the IBOs with Ni, directly correlates with the Hammett σ-values.

This finding reveals that the experimentally observed trend by Sanford and co-workers is not based on the transfer of an electrophilic CF_3 group, but rather the transfer of an aryl cation to a CF_3 anion. Since the cationic character of the aryl group originates from the high-covalency of the Ni–C_{Ar} bond, it may be described as a σ-noninnocence-induced masked aryl-cation transfer. Notably, this also means that the elimination process does not occur in a strictly reductive fashion but approaches redox neutrality. We validated this interpretation by carrying out the EOS analysis along the intrinsic reaction coordinate (IRC) for all frames indicated in Figure 5. Again, at all times, the oxidation state is predicted to be + II for the Ni center as shown in Table S10. We should clarify here that for systems with an increased covalency, it might no longer be appropriate to assign integer oxidation states.[8] Therefore, the oxidation state assignments from the EOS method based on a single-reference approach should only be taken as a guide. We would assign the oxidation state to be approaching + II. Nevertheless, we can clearly state that the redox changes at the Ni center do not reflect those required for a formal reductive elimination, warranting our description of this process as an essentially redox-neutral elimination, which may be viewed as a distinct type of elementary organometallic reaction.

Conclusion

In summary, we may therefore conclude that the formal Ni^{IV} complexes reported by Sanford and co-workers are best described as Ni complexes approaching the + II oxidation state arising from oxidation of the ligands due to σ-non-innocence. As a consequence, one should describe the C–C-bond-forming event not as reductive, but best as essentially redox-neutral, which could be understood as a distinct type of elementary organometallic reactions. The example studied here also clearly demonstrates that inverted ligand fields and, by extension, σ-noninnocence are not limited to poly-fluorinated groups, but instead are more general. Furthermore, an electronic-structure analysis directly in terms of bonding and antibonding molecular orbitals—for example, as here obtained with IBOs and vvIBOs directly from first-principles calculations—allows a clear and unambiguous identification of when these cases are present, in contrast to the established analysis of canonical molecular orbitals (HOMO and LUMO), which, in larger or non-symmetric

coordination complexes, are often highly delocalized and not open to direct interpretation. We believe that the present study is barely scratching the surface of σ-noninnocence and there are many more cases to be discovered, especially since the presence of inverted ligand fields is now more broadly suspected for transition-metal complexes in the literature.[26] The effects that these bonding scenarios have on transition-metal-catalyzed reactions can be expected to be of significant relevance.

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Conflict of interest

The authors declare no conflict of interest.

Homolyse · Ligandenfeldinversion · Münzmetalle · Radikale · Trifluormethyl

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Angew. Chem. **2019**, *131*, 13267 – 13273

[1] a) J. Terao, N. Kambe, *Acc. Chem. Res.* **2008**, *41*, 1545 – 1554; b) H. Shiota, Y. Ano, Y. Aihara, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2011**, *133*, 14952 – 14955; c) Y. Aihara, N. Chatani, *J. Am. Chem. Soc.* **2013**, *135*, 5308 – 5311; d) Y. Aihara, N. Chatani, *J. Am. Chem. Soc.* **2014**, *136*, 898 – 901; e) Z. Ruan, S. Lackner, L. Ackermann, *Angew. Chem. Int. Ed.* **2016**, *55*, 3153 – 3157; *Angew. Chem.* **2016**, *128*, 3205 – 3209; f) T. Uemura, M. Yamaguchi, N. Chatani, *Angew. Chem. Int. Ed.* **2016**, *55*, 3162 – 3165; *Angew. Chem.* **2016**, *128*, 3214 – 3217; g) X. Yang, G. Shan, L. Wang, Y. Rao, *Tetrahedron Lett.* **2016**, *57*, 819 – 836; h) E. Chong, J. W. Kampf, A. Ariafard, A. J. Canty, M. S. Sanford, *J. Am. Chem. Soc.* **2017**, *139*, 6058 – 6061.

[2] J. R. Bour, N. M. Camasso, M. S. Sanford, *J. Am. Chem. Soc.* **2015**, *137*, 8034 – 8037.

[3] a) R. C. Walroth, J. T. Lukens, S. N. MacMillan, K. D. Finkelstein, K. M. Lancaster, *J. Am. Chem. Soc.* **2016**, *138*, 1922 – 1931; b) F. D'Accriscio, P. Borja, N. Saffon-Merceron, M. Fustier-Boutignon, N. Mézailles, N. Nebra, *Angew. Chem. Int. Ed.* **2017**, *56*, 12898 – 12902; *Angew. Chem.* **2017**, *129*, 13078 – 13082; c) I. DiMucci, K. Lancaster, M. Sanford, INOR 406 in *Abstracts of Papers of the American Chemical Society, Vol. 255*, **2018**.

[4] C. C. Roberts, N. M. Camasso, E. G. Bowes, M. S. Sanford, *Angew. Chem. Int. Ed.* **2019**, *58*, 9104 – 9108; *Angew. Chem.* **2019**, *131*, 9202 – 9206.

[5] a) R. Hoffmann, S. Alvarez, C. Mealli, A. Falceto, T. J. Cahill, T. Zeng, G. Manca, *Chem. Rev.* **2016**, *116*, 8173 – 8192; b) G. Aullón, S. Alvarez, *Theor. Chem. Acc.* **2009**, *123*, 67 – 73; c) T. Zeng, K. M. Lancaster, N. Ananth, R. Hoffmann, *J. Organomet. Chem.* **2015**, *792*, 6 – 12.

[6] a) J. P. Snyder, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 80 – 81; *Angew. Chem.* **1995**, *107*, 112 – 113; b) M. Kaupp, H. G. von Schnering, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 986 – 986; *Angew. Chem.* **1995**, *107*, 1076 – 1076; c) J. P. Snyder, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 986 – 987; *Angew. Chem.* **1995**, *107*, 1076 – 1077; d) S. N. MacMillan, K. M. Lancaster, *ACS Catal.* **2017**, *7*, 1776 – 1791; e) C. Gao, G. Macetti, J. Overgaard, *Inorg. Chem.* **2019**, *58*, 2133 – 2139.

[7] M. Baya, D. Joven-Sancho, P. J. Alonso, J. Orduna, B. Menjón, *Angew. Chem. Int. Ed.* **2019**, https://doi.org/10.1002/anie.201903496; *Angew. Chem.* **2019**, https://doi.org/10.1002/ange.201903496.

[8] For recent discussions on oxidation states see: a) P. Karen, *Angew. Chem. Int. Ed.* **2015**, *54*, 4716 – 4726; *Angew. Chem.* **2015**, *127*, 4798 – 4809; b) V. Postils, C. Delgado-Alonso, J. M. Luis, P. Salvador, *Angew. Chem. Int. Ed.* **2018**, *57*, 10525 – 10529; *Angew. Chem.* **2018**, *130*, 10685 – 10689.

[9] C. K. Jørgensen, *Coord. Chem. Rev.* **1966**, *1*, 164 – 178.

[10] For representative reviews on noninnocence and redox-active ligands see: a) W. Kaim, B. Schwederski, *Coord. Chem. Rev.* **2010**, *254*, 1580 – 1588; b) P. J. Chirik, K. Wieghardt, *Science* **2010**, *327*, 794; c) W. Kaim, *Eur. J. Inorg. Chem.* **2012**, 343 – 348; d) V. Lyaskovskyy, B. de Bruin, *ACS Catal.* **2012**, *2*, 270 – 279; e) S. Blanchard, E. Derat, M. Desage-El Murr, L. Fensterbank, M. Malacria, V. Mouriès-Mansuy, *Eur. J. Inorg. Chem.* **2012**, 376 – 389; f) O. R. Luca, R. H. Crabtree, *Chem. Soc. Rev.* **2013**, *42*, 1440 – 1459; g) D. L. J. Broere, R. Plessius, J. I. van der Vlugt, *Chem. Soc. Rev.* **2015**, *44*, 6886 – 6915; h) A. Chirila, B. G. Das, P. F. Kuijpers, V. Sinha, B. d. Bruin in *Non-Noble Metal Catalysis* (Eds.: R. J. K. Gebbink, M. Moret), Wiley-VCH, Weinheim, **2019**, https://doi.org/10.1002/9783527699087.ch9783527699081; for a discussion on the distinction between noninnocence and redox-active ligands see: i) P. J. Chirik, *Inorg. Chem.* **2011**, *50*, 9737 – 9740.

[11] Y. Zhao, D. G. Truhlar, *J. Chem. Phys.* **2006**, *125*, 194101.

[12] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297 – 3305.

[13] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378 – 6396.

[14] E. Ramos-Cordoba, V. Postils, P. Salvador, *J. Chem. Theory Comput.* **2015**, *11*, 1501 – 1508.

[15] D. Rappoport, F. Furche, *J. Chem. Phys.* **2010**, *133*, 134105.

[16] As an alternative interpretation, the authors of the original experimental study suggested that loss of the ligand *trans* to the aryl moiety could lead to a highly reactive five-coordinate intermediate. We have computed this pathway as well and find it to be significantly higher in energy. The data can be found in the Supporting Information.

[17] G. Knizia, *J. Chem. Theory Comput.* **2013**, *9*, 4834 – 4843.

[18] a) J. E. M. N. Klein, B. Miehlich, M. S. Holzwarth, M. Bauer, M. Milek, M. M. Khusniyarov, G. Knizia, H.-J. Werner, B. Plietker, *Angew. Chem. Int. Ed.* **2014**, *53*, 1790 – 1794; *Angew. Chem.* **2014**, *126*, 1820 – 1824; b) J. E. M. N. Klein, G. Knizia, B. Miehlich, J. Kästner, B. Plietker, *Chem. Eur. J.* **2014**, *20*, 7254 – 7257; c) L. Nunes dos Santos Comprido, J. E. M. N. Klein, G. Knizia, J. Kästner, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2015**, *54*, 10336 – 10340; *Angew. Chem.* **2015**, *127*, 10477 – 10481; d) L. Nunes dos Santos Comprido, J. E. M. N. Klein, G. Knizia, J. Kästner, A. S. K. Hashmi, *Chem. Eur. J.* **2016**, *22*, 2892 – 2895; e) J. E. M. N. Klein, R. W. A. Havenith, G. Knizia, *Chem. Eur. J.* **2018**, *24*, 12340 – 12345; f) D. Sorbelli, L. Nunes dos Santos Comprido, G. Knizia, A. S. K. Hashmi, L. Belpassi, P. Belanzoni, J. E. M. N. Klein, *ChemPhysChem* **2019**, https://doi.org/10.1002/cphc.201900411.

[19] a) G. Knizia, http://www.iboview.org/; b) G. Knizia, J. E. M. N. Klein, *Angew. Chem. Int. Ed.* **2015**, *54*, 5518 – 5522; *Angew. Chem.* **2015**, *127*, 5609 – 5613.

[20] S. Ye, C.-Y. Geng, S. Shaik, F. Neese, *Phys. Chem. Chem. Phys.* **2013**, *15*, 8017 – 8030.
[21] It is worth mentioning that the localization of MOs renders their energetic ordering obsolete. Nevertheless, since the occupied and virtual MOs are transformed to IBOs separately, evaluation of the localized virtual space can be readily used to probe if an inverted ligand field is present.
[22] C. N. Neumann, J. M. Hooker, T. Ritter, *Nature* **2016**, *534*, 369 – 373.
[23] E. V. Anslyn, D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, Sausalito, **2006**.
[24] a) J. E. M. N. Klein, G. Knizia, L. Nunes dos Santos Comprido, J. Kästner, A. S. K. Hashmi, *Chem. Eur. J.* **2017**, *23*, 16097 – 16103; b) L. Nunes Dos Santos Comprido, J. E. M. N. Klein, G. Knizia, J. Kästner, A. S. K. Hashmi, *Chem. Eur. J.* **2017**, *23*, 10901 – 10905; c) J. E. M. N. Klein, G. Knizia, *Angew. Chem. Int. Ed.* **2018**, *57*, 11913 – 11917; *Angew. Chem.* **2018**, *130*, 12089 – 12093.
[25] I. Fernández, G. Frenking, *J. Org. Chem.* **2006**, *71*, 2251 – 2256.
[26] a) S. Mukherjee, D. E. Torres, E. Jakubikova, *Chem. Sci.* **2017**, *8*, 8115 – 8126; b) S. Ruccolo, M. Rauch, G. Parkin, *Chem. Sci.* **2017**, *8*, 4465 – 4474; c) H. D. Nelson, S. O. M. Hinterding, R. Fainblat, S. E. Creutz, X. Li, D. R. Gamelin, *J. Am. Chem. Soc.* **2017**, *139*, 6411 – 6421; d) S.-X. Hu, W.-L. Li, J.-B. Lu, J. L. Bao, H. S. Yu, D. G. Truhlar, J. K. Gibson, J. Marçalo, M. Zhou, S. Riedel, W. H. E. Schwarz, J. Li, *Angew. Chem. Int. Ed.* **2018**, *57*, 3242 – 3245; *Angew. Chem.* **2018**, *130*, 3297 – 3300; e) L. Li, T. Stüker, S. Kieninger, D. Andrae, T. Schlöder, Y. Gong, L. Andrews, H. Beckers, S. Riedel, *Nat. Commun.* **2018**, *9*, 1267; f) J. E. Terán, C. H. Zambrano, J. R. Mora, L. Rincón, F. J. Torres, *J. Mol. Model.* **2018**, *24*, 316; g) B. J. Cook, G. N. Di Francesco, R. B. Ferreira, J. T. Lukens, K. E. Silberstein, B. C. Keegan, V. J. Catalano, K. M. Lancaster, J. Shearer, L. J. Murray, *Inorg. Chem.* **2018**, *57*, 11382 – 11392; h) D. Joven-Sancho, M. Baya, A. Martín, B. Menjón, *Chem. Eur. J.* **2018**, *24*, 13098 – 13101; i) J. T. Lukens, I. M. DiMucci, T. Kurogi, D. J. Mindiola, K. M. Lancaster, *Chem. Sci.* **2019**, *10*, 5044 – 5055.

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